STUDIES ON METHANOL CROSSOVER IN LIQUID-FEED DIRECT METHANOL PEM FUEL CELLS

S. R. Narayanan, H. Frank, B. Jeffries-Nakamura, M. Smart, W. Chun and G. Halpert
Jet Propulsion Laboratory, California Institute of Technology,
4800 Oak Grove Drive, Pasadena, CA 91109

J. Kosek and C. Cropley
Giner Inc., 14 Spring Street, Waltham, MA 02154

Abstract

The performance of liquid feed direct methanol fuel cells using various types of Nafion membranes as the solid polymer electrolyte have been studied. The rate of fuel crossover and electrical performance has been measured for cells with Nafion membranes of various thicknesses and equivalent weights. The crossover rate is found to decrease with increasing thickness and applied current . The dependence of crossover rate on current density can be understood in terms of a simple linear diffusion model which suggests that the crossover rate can be influenced by the electrode structure in addition to the membrane. The studies suggest that Nation EW 1500 is a very promising alternate to Nafion EW 1100 for direct methanol fuel cells.

Introduction

A liquid-feed type direct methanol fuel cell using proton-exchange membrane electrolyte was developed under an ARPA-sponsored program and is now being actively considered by DOE and DOD for stationary, portable, and transportation applications[1-3]. This fuel cell operates on aqueous solutions of methanol as fuel and oxygen or air as the oxidant and uses an ionically conducting polymer membrane such as Nafion® 117 as the electrolyte. This type of direct oxidation cell is fuel versatile and offers significant advantages in terms of simplicity of design and operation. In order to improve the performance of these cells, it is necessary to reduce the parasitic loss of fuel across the cell, termed "fuel crossover". The present study on fuel crossover focuses on Nafion® type membranes of various thicknesses and equivalent weight. The effect of applied current density on fuel crossover has also been studied,

Experimental approach

The membrane-electrode assemblies used in this study had an active area of 25 cm^2. The anode consisted of 4 mg/cm^2 of Pt-Ru and the cathode of 1 mg/cm^2 of Pt and were fabricated by Giner, Inc. The catalyzed electrodes were bonded to the various Nafion-type membranes supplied by Du Pent. Crossover rates were measured by estimating the carbon dioxide content of the cathode exit stream using a Horiba VIA-5 10 Analyzer. The

methanol concentration was maintained at 1 M in all the experiments. Crossover rate is reported as an equivalent current density of methanol oxidation. Crossover rate was measured under open circuit and on load. Nafion types of various equivalent weights and thicknesses were investigated.

Results and Discussion

Results presented in Fig 1 show that membrane thickness has a significant impact on crossover. Increasing the thickness from 5 roils to 14 mils causes the crossover to reduce by about 40-50%. At the operating current density of 300 mA/cm^2, the reduction in crossover rate with thickness is about 10.5 mA/cm^2 per mil of reduction in thickness. This can be used as a value for first approximation in estimating crossover reduction by increasing membrane thickness.

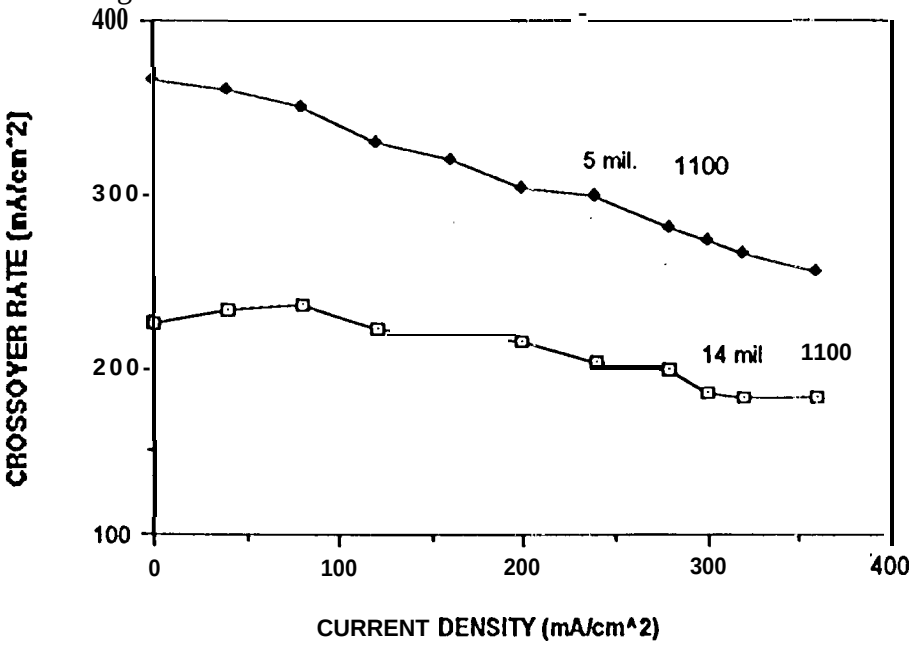
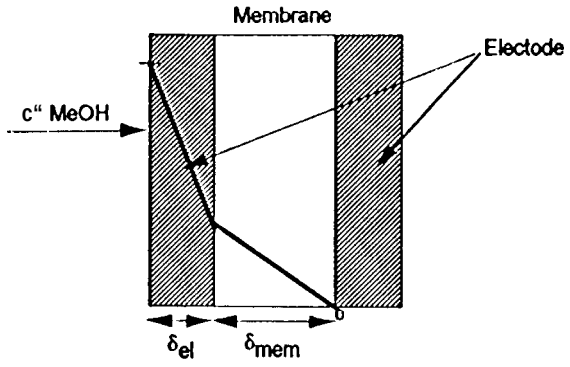
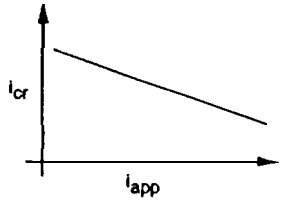


Fig. 1. Effect of membrane thickness on crossover for Nafion EW 1100.

Under actual conditions of operation, the crossover rate decreases with increasing current density of operation. From Fig, 1 it is seen that this effect is similar for membranes of two different thicknesses. Initially, it was perceived that methanol crossover phenomena was controlled only by transfer of methanol through the membrane. However, the results , shown in Fig. 1 suggests that factors other than membrane thickness govern the effect of applied load on crossover. A phenomenological linear diffusion model for the steady-state conditions prevailing during fuel cell operation was presented earlier [4] and considered only membrane effects. This model can now be extended to include electrode effects is shown in Fig.2.



i_{app} = applied current density
i_{cr} = crossover current density
D_{el} = apparent diffusion coefficient in the electrode structure
D_{mem} = apparent diffusion coefficeint in the membrane
A = area
F = Faraday
n = number of electrons/ mole
c = concentration of MeOH at the inlet
c = concentration of MeOH adjacent to the edge of membrane



The flux of methanol across the electrode structure is related to the total current as follows:

$$i_{app} + i_{cr} = nFAD_{el}(C^*-C)/\delta_{el}$$

The flux of methanol due to crossover is given by,

$$i_{cr} = nFAD_{mem}C/\delta_{mem}$$

Combining the above relations,

$$i_{cr}=nFAD_{el}\{1/(1+k)\}C^*/\delta_{el} - i_{app}\{1/(1+k)\}$$

where $k=D_{el}\delta_{mem}/(D_{mem}\delta_{el})$

Fig.2: Phenomenological modelling of the crossover of methanol across the membrane electrode assembly

The methanol concentration is shown to vary from a known inlet value to an intermediate value on the fuel side and then finally to known zero concentration on the cathode. In the steady state all these concentration gradients are linear. The methanol consumption rate in the electrode in terms of the measured current and concentration gradient in the electrode structure is related to the methanol crossover rate through the membrane to yield an expression for crossover rate of methanol in terms of membrane and electrode properties and applied current. Such a model explains the apparent linear decrease in crossover rate with current density and suggests that the crossover can be reduced by altering the methanol permeabilities of the catalyst layer and electrode structure.

The electrical performance of fuel cells with 1100 EW membrane of various thicknesses (Fig.3) shows that the performance trend is probably determined by the combined effects of ionic conductivity and fuel crossover. As a result at higher thicknesses, the ohmic resistance of the cell could be determining the cell voltage, although there would have been some enhancement of the cell voltage due to reduced crossover,

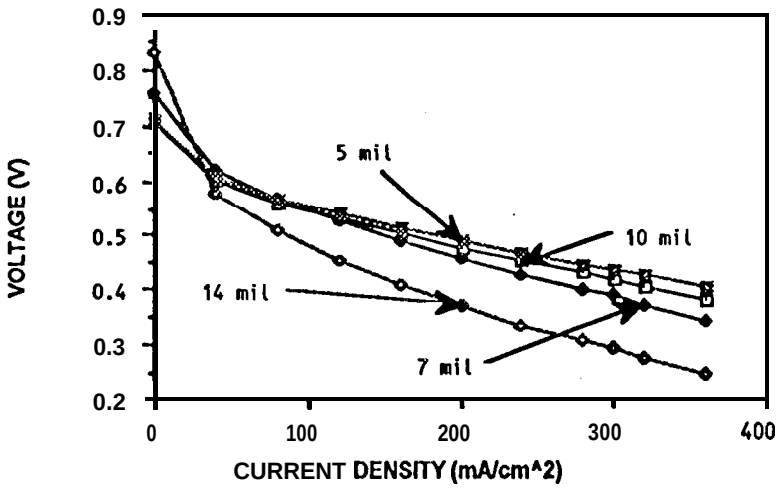


Fig.3: Electrical performance of direct methanol fuel cells with Nation 1100 membranes of various thicknesses.

Results presented in Fig. 4 demonstrate that high equivalent weight Nafion-types exhibit lower methanol permeability.

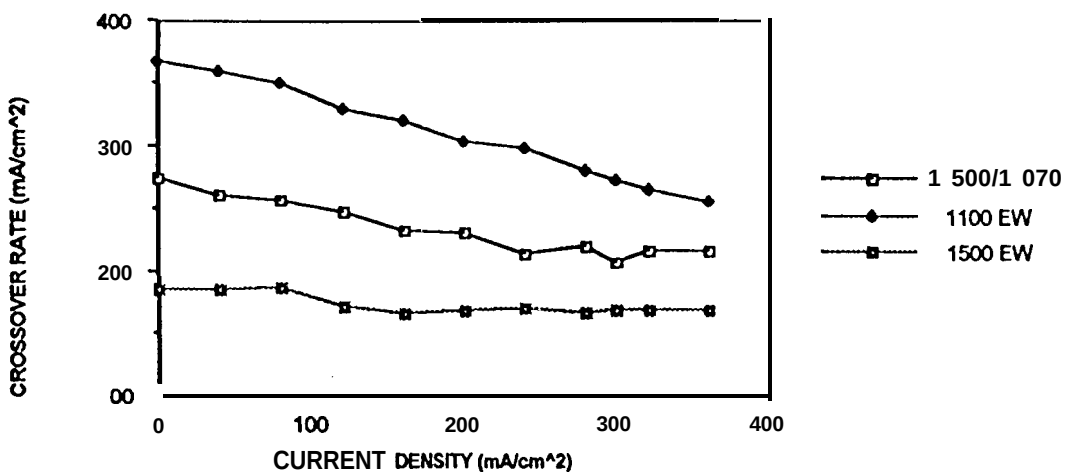


Fig. 4: Crossover rate in direct methanol fuel cells with Nafion membranes of different equivalent weight types

Electrical performance studies (Figure 5) on various membranes of different equivalent weights indicates a small reduction in voltage and increase in slope with in-creasing membrane equivalent weight.

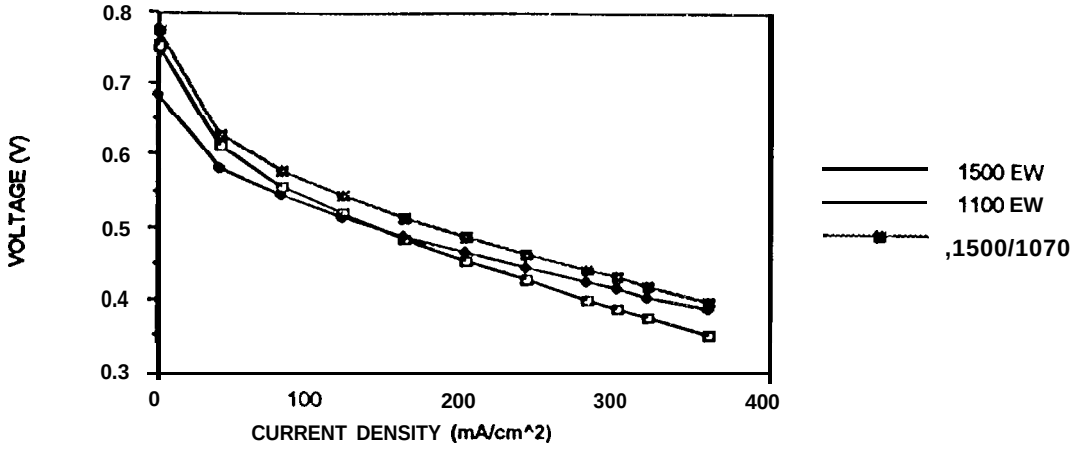


Fig.5: Electrical Performance of direct methanol fuel cells with Nafion 1500 and 1100.

These findings are consistent with the results of ionic conductivity measurements (Figure 6) suggesting that Nafion 1500 would be a promising alternate to Nafion 1100. The Nation membrane consisting of a thin layer of EW 1500 and a thicker layer of EW 1070 shows an intermediate crossover rates and electrical performance.

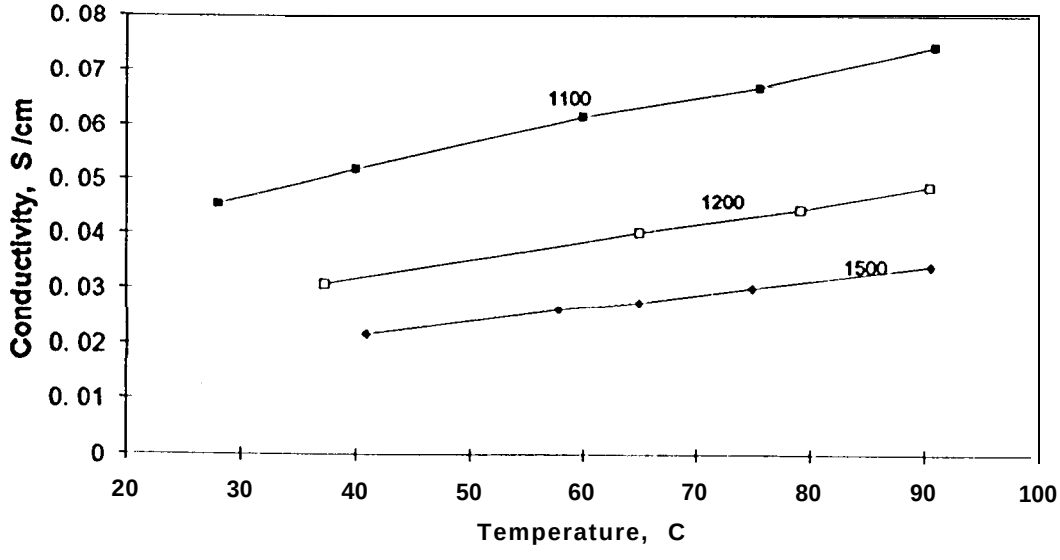


Fig.6: Electrical conductivity of Nafion membranes of different equivalent weights.

The open circuit voltage of the cells with various membrane types correlated with the crossover rate as shown in Table 1.

Table 1: Open circuit voltage of methanol/oxygen fuel cell with 1 M methanol at 900C

MEMBRANE TYPE, EW	CROSSOVER RATE, mA/cm2	OCV
1100	313	0.748
(1500/1070)	275	0.755
1200	227	0.766
1500	186	0.778

The cell voltage decreases with increasing crossover rate. Similar effects on the on-load voltage of the cell is to be expected.

Acknowledgments:
The work presented here was carried out at the Jet Propulsion Laboratory, California Institute of Technology, in a program sponsored by ARPA under a contract with the National Aeronautics and Space Administration.

References:

1. S. Surampudi, S. R. Narayanan, E. Vamos, H. Frank and G.Halpert, J. Power Sources, 47(1994) 377-385.

2. S. R. Narayanan, E. Vamos, S. Surampudi, H. Frank and G. Halpert, Presented at the Fuel Cell Seminar, Nov 29-Dec 2, 1992, Tucson, AZ.

3. J. Kosek, C.C. Cropley, A. B. La Conti, G. Wilson, S. R. Narayanan, E. Vamos, S. Surampudi and H. Frank, Proceedings of theIECEC 1993, Volume 1, p. 1209.

4. S. R. Narayanan, E. Vamos, S. Surampudi, H. Frank and G. Halpert, Presented at the Electrochemical Society Meeting, New Orleans, LA, October 10-15, 1993, Abstract 73.